Quasi-one-dimensional spin chains in $CuSiO_3$: an EPR study

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Temperature dependent EPR studies were performed on a single crystal of $CuSiO_3$. This recently discovered compound is isostructural with the spin-Peierls compound $CuGeO_3$. The EPR signals show different characteristics than those of $CuGeO_3$ and are due to Cu^{2+} spins located along quasi one-dimensional chains. For $T > 8.2$ K the spin susceptibility closely follows the predictions of a $S = 1/2$ one-dimensional Heisenberg antiferromagnet with $J/k_B = 21$ K. Below $T = 8.2$ K the spin susceptibility immediately drops to zero indicating long range magnetic order.

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The linear spin-chain system $CuGeO_3$ is the first and up to now the only inorganic compound that exhibits a spin-Peierls transition.[1] Regarding the magnetic properties the partial substitution of Ge by Si was an important subject in terms of studying frustration effects[2] and the coexistence of the spin-Peierls state with long-range antiferromagnetic order.[3,4] To characterize the nature of antiferromagnetic interactions in Si doped and pure $CuGeO_3$ electron paramagnetic resonance (EPR) of Cu^{2+} spins provided important results.[5–8] In pure $CuGeO_3$ the EPR parameters differ from those of conventional one-dimensional Heisenberg antiferromagnets. The antisymmetric Dzyaloshinsky-Moriya (DM) exchange interaction was claimed to explain this difference.[6] In Si doped $CuGeO_3$ coexistence of spin-Peierls and antiferromagnetic order is reported for Si concentrations below $\approx 1\%$. For higher Si concentrations (up to 50%) a long range antiferromagnetic ground state is observed.[4] However, for $T > 15$ K the temperature dependence of the EPR parameters does not change significantly for Si-doping concentrations up to 7%.[7,8] This paper reports the first EPR results on pure $CuSiO_3$ which are very different from pure and slightly Si-doped $CuGeO_3$.

The EPR measurements were performed at X-band frequency with a Bruker ELEXSYS spectrometer. For cooling a continuous-flow helium cryostat (Oxford) was used. The spectra were taken from a non-oriented single crystal of $CuSiO_3$ at temperatures between 4 K and 300 K. DC magnetization measurements at low fields $H \leq 10$ kOe were carried out on a commercial SQUID magnetometer.[9] The single crystal of $CuSiO_3$ was synthesized by dehydration of the mineral dioptase.[10] Reported EPR spectra of CuO[11] did not show up in our EPR spectra which indicated the high quality of our crystal. Figure 1 shows the temperature dependence of the EPR linewidth and EPR g factor (determined from the EPR resonance field) of the investigated $CuSiO_3$ crystal. The inset of Fig. 1 shows a representative EPR spectrum of $CuSiO_3$ at $T = 40$ K (solid line, derivative of the EPR absorbed power). At all temperatures the spectra could be nicely fitted with a Lorentzian derivative (dashed line in the inset of Fig. 1).

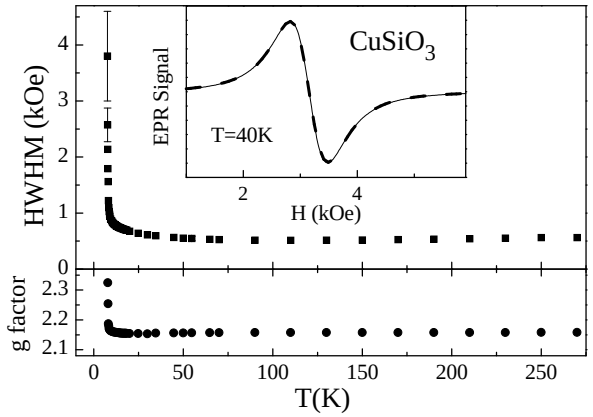

FIG. 1. Temperature dependence of EPR linewidth (HWHM) and EPR g factor, determined by the resonance field. Inset: typical EPR spectrum (derivative of absorbed power, solid line) and Lorentzian line fit (dashed line).

The EPR linewidth linearly decreases down to $T \approx 100$ K at a rate 0.5 Oe/K. This contrasts to a much steeper and non-linear decrease of the linewidth in $CuGeO_3$ which the antisymmetric DM interaction was used for to explain the linewidth.[5,6] Therefore in $CuSiO_3$ a DM interaction seems to be less important. Anisotropic exchange interactions also contribute to the EPR linewidth. As the deviation of the O(2)-Cu-O(2) angle from 90° is smaller in $CuSiO_3$ than in $CuGeO_3$[4,10] the anisotropic exchange interactions in both compounds should be different.[12] For temperatures above $T \approx 12$ K

the EPR g factor has a nearly temperature independent value of $g = 2.156 \pm 0.001$ which is commonly observed for Cu^{2+}-ions in an octahedral environment. This is consistent with the crystal structure of $CuSiO_3$ which is reported to be the same as in $CuGeO_3$ (orthorhombic, *Pbmm*) and where the Cu^{2+}-ions are located within strongly elongated oxygen octahedra.[10]

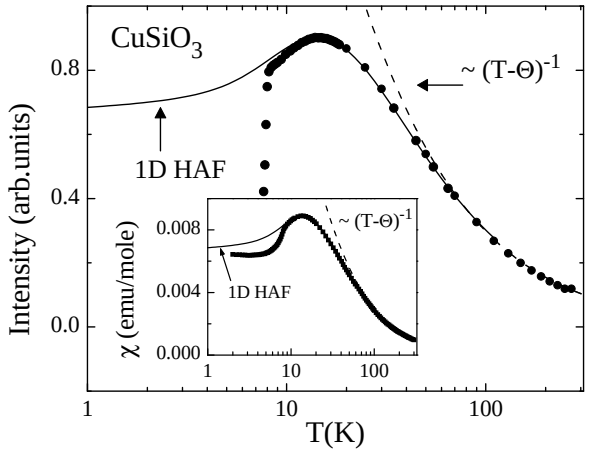

FIG. 2. Temperature dependence of the EPR intensity (integrated EPR signal, solid circles). Inset: Magnetic susceptibility vs. temperature.[9] The solid lines represent the behavior of an one-dimensional Heisenberg antiferromagnet with $S = 1/2$.[13] The dashed lines are Curie-Weiss laws with $\Theta = -7.2$ K.

Figure 2 shows the temperature dependence of the EPR intensity $I_{EPR}(T)$ which is determined by integration of the spectra. $I_{EPR}(T)$ is proportional to the spin susceptibility of Cu^{2+} and can be well compared with the magnetic susceptibility $\chi(T)$[9] as shown in the inset of Fig. 2. However, below $T = 8.24$ K the EPR intensity reduces rapidly to zero, indicating an ordering phenomenon rather than a spin-Peierls state which produces an exponential decrease of the intensity.[5] This is also evidenced by the none vanishing $\chi(T \to 0)$ which is usually due to an anisotropic antiferromagnetic state.[9] Above $T = 8.2$ K $\chi(T)$ and $I_{EPR}(T)$ are very well described by theoretical calculations for an $S = 1/2$ one-dimensional Heisenberg antiferromagnet (1D HAF) without frustration effects.[13] This leads to an Cu-O(2)-Cu exchange of $J/k_B = 21$ K which is much smaller than in $CuGeO_3$ ($J/k_B \approx 160$ K) as can be expected from the smaller Cu-Cu distances and the smaller O(2)-Cu-O(2) in $CuSiO_3$.[4,10] For high temperatures $\chi(T)$ and $I_{EPR}(T)$ nicely follow a Curie-Weiss law with a Weiss-temperature of $\Theta = -7.2$ K, indicating weak antiferromagnetic coupling.

Figure 3 shows a characterization of the temperature dependence of the EPR linewidth. The high temperature part is estimated with a linear function $\Delta H_{lin}(T) = 0.5 \cdot T$ Oe/K + 300 Oe. This linear part was subtracted from ΔH in order to obtain the broadening ΔH_{crit} when the temperature is lowered towards a critical temperature $T_{crit} = 7.5$ K. A power law $\Delta H_{crit} \propto (T - T_{crit})^{-\alpha}$ approximately describes the linewidth with $\alpha = 0.25$ at low temperatures and above $T = 8.2$ K. However, at $T \approx 8.2$ K the type of broadening obviously changes as a noticeable deviation from a power law occurs. This is indicated by the short dashed line in Fig. 3. The linewidth strongly increases nearly below the same temperature ($T \approx 8.2$ K) where a strong increase of the g factor is observed as well (see Fig. 1). Hence the change of line broadening is indicative for the onset of magnetic ordering which yields strong internal fields and therefore inhomogeneous line broadening effects. Measurements of the specific heat give strong evidence for long range antiferromagnetic order.[9] From the critical behavior of the linewidth it is not possible to compare $CuSiO_3$ unambiguously with typical antiferromagnets neither for the one-dimensional case like $CuCl_2{\cdot}2NC_5H_5$ ($\alpha = 0.5$)[14] nor for the three-dimensional case like GdB_6 ($\alpha = 1.5$)[15].

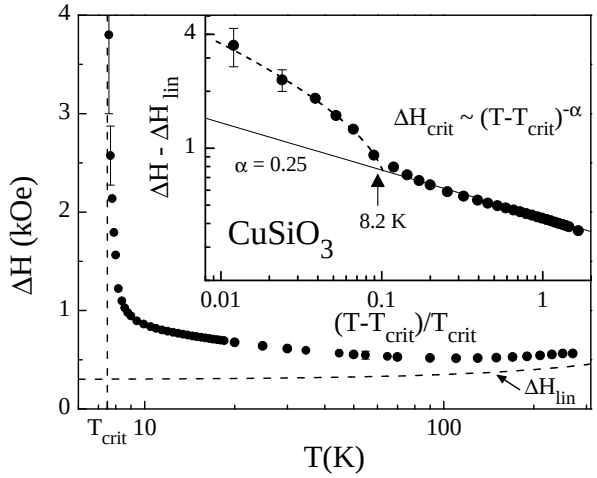

FIG. 3. Temperature behavior of the EPR linewidth ΔH: at high T the dashed line approximates the linewidth with a linear function ΔH_{lin}. The inset displays the reduced linewidth $\Delta H - \Delta H_{lin}$ vs. reduced temperature $(T - T_{crit})/T_{crit}$ ($T_{crit} = 7.5$ K) in order to characterize the critical line broadening ΔH_{crit}. The solid line represents a power law according to $\Delta H_{crit} \propto (T - T_{crit})^{-\alpha}$.

In summary our EPR results on $CuSiO_3$ do not show evidences for a spin-Peierls state below $T = 8.2$ K. For low temperatures the EPR intensity and EPR linewidth are rather explained by long-range magnetic ordering phenomena. For temperatures above $T = 8.2$ K the EPR intensity is proportional to the magnetic susceptibility and can be reproduced well with a behavior of an one-dimensional antiferromagnet. Antisymmetric and anisotropic exchange interactions contribute differently to the EPR parameters in $CuSiO_3$ and $CuGeO_3$. Further clarification should be provided by measurements at higher temperatures and at defined crystal orientations which presently are in progress.

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